DOI 10.1007/s10717-014-9653-7
Glass and Ceramics, Vol. 71, Nos. 5 – 6, September, 2014 (Russian Original, Nos. 5 – 6, May – June, 2014)

UDC 666.293.522.53

PHASE COMPOSITION OF THE PRODUCTS OF COMBUSTION OF FERROALUMINUM SILICON IN NITROGEN IN THE PRESENCE OF FLUORINE CONTAINING ADDITIVES

L. N. Chukhlomina[1] and K. A. Bolgaru[1, 2]

Translated from *Steklo i Keramika*, No. 6, pp. 25 – 27, June, 2014.

The results of an investigation of the combustion of ferroaluminum silicon (FAS) in nitrogen in the presence of fluorine-containing additives are presented. The phase composition of the products of combustion is studied. It is shown that the introduction of fluorine-containing additives to the initial alloy significantly increases the degree of nitriding (to 27.2%).

Key words: self-propagating high-temperature synthesis, nitriding, silicon nitride, â-SiAlON, fluorine-containing additive.

Possessing high porosity, heat resistance and chemical inertness with respect to many aggressive media silicon nitride and materials based on it are promising for use in different areas of modern technology. In recent years silicon nitride and materials based on it have been synthesized using ferrosilicon alloys as the initial reagents [1].

The process of nitriding complex alloys containing several nitride-forming elements is of special interest. A promising method for obtaining nitrides is self-propagating high-temperature synthesis (SHS), which is distinguished by high efficiency and low energy consumption, which is very important in industrial production. For example, it is shown in [2] that the alloy ferroaluminum silicon (FAS) can be used as the initial material to obtain metal-ceramic compositions based on silicon nitride and â-SiAlON by means of SHS. The combustion processes proceeds in a nonstationary regime, and the nitrogen content in the products of synthesis in the absence of additives does not exceed 22.5%.[3]

It is known that the nitrogen content in the products of SHS can be increased by means of different kinds of additives: inert, gasifying and activating the nitriding process. Usually, ammonium salts, which on decomposition form the additional nitriding agent NH_3, are used. It is shown in [4] that ammonium fluoride and topaz concentrate make it possible to increase the degree of nitriding of ferrosilicon to 100%.

The aim of the present work is to investigate the influence of fluorine-containing additives on the phase composition of the products of combustion of the complex alloy ferroaluminum silicon (FAS) in nitrogen.

The initial material was FS65A15 grade FAS. X-ray phase analysis (XPA) was performed with a DRON-2 diffractometer using Co radiation and shows the initial FAS to be a monophase material consisting of silicon and high-temperature lebeauite $FeSi_2$. X-ray spectral microanalysis of the initial ferroaluminum silicon showed that the aluminum is mainly found in the solid solution based on $FeSi_2$, forming two phases with different ratio of silicon and aluminum: $FeSi_{2.2}Al_{0.4}$ and $FeSi_{1.6}Al_{2.2}$. The phases Al_2O_3 and $Al_{0.5}Fe_{0.5}$ are present as impurities. Chemical analysis shows the alloy consists of 60.1% silicon, 13.2% aluminum and 26.7% iron.

Ammonium fluoride NH_4F (chemically pure grade) and topaz concentrate were used as fluorine-containing additives. The topaz additive (Kopna deposit in Kemerovo Oblast') is a natural fluoroaluminosilicate $Al_2SiO_4(F, OH)_2$ with the following composition (%): SiO_2 – 40.98; Al_2O_3 – 34.98; Fe_2O_3 – 2.36; $(H_2O + F)$ – 19.1; CaO – 1.4; and, Mg – 1.2. Before SHS was conducted the FAS powder with particle size < 100 μm was dried in a vacuum desiccator at temperature 150 – 200°C to remove moisture and volatile impurities. Next, the iron alloy powder was mixed with a fluorine-containing additive and poured into cylindrical tubes made of metal mesh with diameter 40 mm. The samples were placed

[1] Division of Structural Macrokinetics, Tomsk Scientific Center, Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia.
[2] National Research Tomsk Polytechnical University, Tomsk, Russia (e-mail: kbolgaru2008@yandex.ru).
[3] Here and below, the content by weight, %.

0361-7610/14/0506-0205 © 2014 Springer Science+Business Media New York

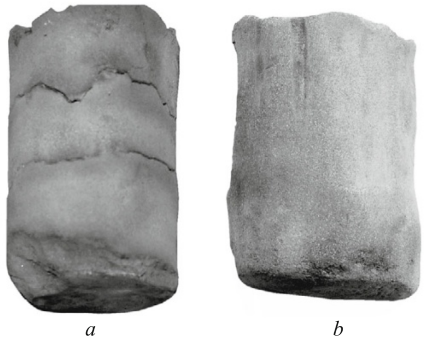

Fig. 1. Product of combustion of FAS in nitrogen without additives (*a*) and with 0.3% topaz concentrate (*b*): p_{N_2} = 4 MPa; *d* = 40 mm.

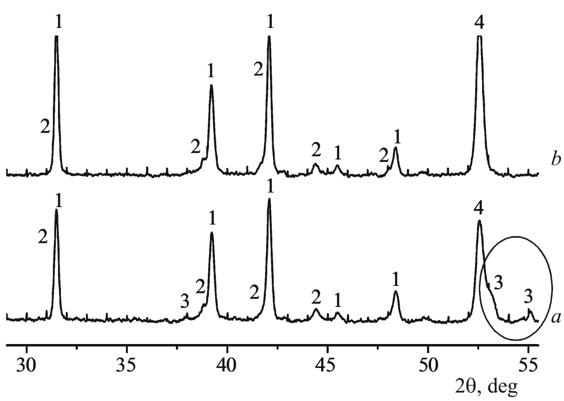

Fig. 2. Phase composition of the products of combustion of FAS in nitrogen in the presence of additions of topaz concentrate: *a*) 0.3%; *b*) 1.5%; peaks: *1*) β-Si_3N_4; *2*) $Si_3Al_3O_3N_5$; *3*) Fe_5Si_3; *4*) Fe.

in a constant-pressure setup and burned in a nitrogen atmosphere at pressure 4 MPa. Ignition was performed from a powdered detonating mixture using a tungsten coil, through which an electric current was passed. After the combustion front passed, the sample was kept in a nitrogen atmosphere to complete cooling, after which the pressure was relieved and the product of SHS was removed from the setup for study.

As noted above, FAS burns in nitrogen in a nonstationary regime. The experiments showed that the introduction into FAS of a topaz concentrate in amounts 0.3 – 1.5% transforms the nonstationary regime of combustion (Fig. 1*a*) into a layered regime (Fig. 1*b*). Here, the burned sample has a more uniform macrostructure and transverse cracks, which are due to melting and shrinkage of the initial alloy, are eliminated. The propagation of the wave of combustion in the layer regime is preferable, since in this case the phase composition of the products of combustion is more uniform and possesses a higher degree of nitriding.

According to XPA the products of combustion of FAS with the addition of 0.3% topaz concentrate are represented by the following phases: β-Si_3N_4, β-$Si_3Al_3O_3N_5$, Fe_5Si_3 and α-Fe. The presence of iron silicide Fe_5Si_3 in the products of combustion indicates that the nitride formation process is incomplete. When topaz concentrate is added in the amount 1.5% to the initial batch, there are virtually no reflections of the silicide phases (Fig. 2*a*), which indicates that the nitride formation reaction goes farther to completion (Fig. 2*b*). This is also indicated by the increase in the α-Fe reflections in the presence of topaz in the amount 1.5%.

The mechanism of the action of the topaz concentrate is due to the physical and chemical processes occurring in the combustion wave. The topaz in front of the combustion front is subjected to thermal destruction, as a result of which mullite, silica in the form of cristobalite and hydrogen fluoride gas are formed [5]:

$$6[Al_2SiO_4(F, OH)_2] \rightarrow 2[3Al_2O_3 \cdot 2SiO_2] + 2SiO_2 + 6HF.$$

At higher temperatures the hydrogen fluoride interacts with silicon oxide:

$$SiO_2 + 4HF \rightarrow SiF_4\uparrow + H_2O.$$

At 1800°C the mullite melts and decomposes, and corundum is precipitated. In the combustion process silicon tetrafluoride is nitrided and silicon nitride is formed according to the scheme

$$SiF_{4(g)} + Si_{(s)} \rightarrow 2SiF_{2(g)};$$

$$6SiF_{2(g)} + 2N_2 \rightarrow Si_3N_{4(s)} + 3SiF_{4(g)}.$$

At the completion of the nitriding process the silicon tetrafluoride interacts with iron in a nitrogen atmosphere and iron tetrafluoride is formed:

$$3SiF_{4(g)} + 4Fe + 2N_2 \rightarrow Si_3N_{4(s)} + 4FeF_3.$$

Thus, the gaseous products (HF, SiF_4, SiF_2) formed as a result of the thermal decomposition of the topaz concentrate loosen the sample, facilitating the filtration of nitrogen to the reaction zone, which increases the degree of nitriding.

In contrast to the topaz concentrate, the addition of ammonium fluoride in the amount 0.3% to the initial batch does not change the combustion regime. A stationary combustion regime can be organized by introducing into FAS the additive NH_4F in the amount 0.5 – 1.5%. The XPA data (Fig. 3*a*) show that in the presence of ammonium fluoride the products of combustion do not contain components of the initial ferroaluminum silicate ($FeSi_2$, Si, Al_2O_3, $Al_{0.5}Fe_{0.5}$), and the intensity of the α-Fe reflections is much higher than the corresponding peaks observed in the presence of the topaz concentrate. In addition, it is evident from the diffraction profile that as the amount of ammonium fluoride additive increases, the formation of the SiAlON phase is more intense (Fig. 3*b*). The deeper nitriding is probably due to the fact that in the heating zone ammonium fluoride decomposes into hydrogen fluoride and ammonia. The latter, in turn, is an additional nitriding agent.

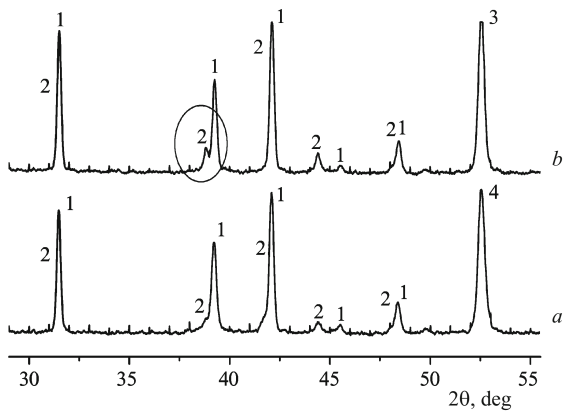

Fig. 3. Phase composition of the products of combustion of FAS in nitrogen in the presence of ammonium fluoride: *a*) 0.3%; *b*) 1.0%; peaks: *1*) β-Si_3N_4; *2*) $Si_3Al_3O_3N_5$; *3*) α-Fe.

These investigations have shown that ammonium fluoride and topaz concentrate can be used to increase the degree of nitriding of FAS. The maximum nitriding is practically the same for both additives and equals 27.2%. The products of combustion of FAS in nitrogen in the presence of topaz concentrate are a loose, practically unsintered, powdery material, which can be used to obtain ceramic materials by well-known methods of compaction (hot pressing, sintering and others). On the other hand the products of nitriding of FAS in the presence of ammonium fluoride possess mechanical strength and can be used as a porous filtering element or an active iron-containing catalyst.

CONCLUSIONS

It was established that the introduction into the initial alloy FAS of fluorine-containing additives transforms the nonstationary regime of combustion into a layer regime. In the process the degree of nitriding increases, reaching 27.2%, which is higher than the degree of nitriding of the alloy with no additives (22.5%). The phase composition of the products of combustion obtained with NH_4F and topaz as additives is qualitatively the same.

REFERENCES

1. L. N. Chukhlomina, "Regularities of the synthesis of silicon nitride by combustion of iron-silicon alloy in nitrogen," *Zh. Prikl. Khim.*, **80**(11), 176 – 177 (2007).
2. L. N. Chukhlomina, K. A. Bolgaru, and V. I. Vereshchagin, "Regularities of the combustion of ferroaluminum silicon in nitrogen," *Izv. Vyssh. Uchebn. Zaved., Fiz.*, No. 7/2, 15 – 19 (2013).
3. G. V. Samsonov, *Nitrides* [in Russian], Naukova Dumka, Kiev (1969).
4. L. N. Chukhlomina, O. G. Vitushkina, and V. I. Vereshchagin, "Phase composition of the products of combustion of ferrosilicon in nitrogen in the presence of fluorine-containing additives," *Steklo Keram.*, No. 7, 22 – 24 (2008); L. N. Chukhlomina, O. G. Vitushkina, and V. I. Vereshchagin, "Phase composition of the products of combustion of ferrosilicon in nitrogen with fluorine-containing additives present," *Glass Ceram.*, **65**(7 – 8), 236 – 239 (2008).
5. T. V. Vakalova, A. V. Ivanchenkov, and V. M. Pogrebenkov, "Activation of solid-phase sintering of mullite by topaz additives," *Novye Ogneupory*, No. 1, 40 – 45 (2005).